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Hydrochlorination of Ruthenaphosphaalkenyls: Unexpectedly Facile Access to Alkylchlorohydrophosphane Complexes.

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Supporting Information Placeholder

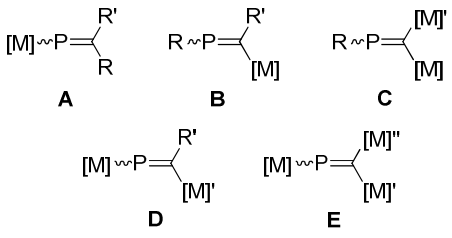
ABSTRACT: The novel ruthenaphosphaalkenyls [Ru{P=C(H)SiMe$_2$R}Cl(CO)(PPh$_3$)$_2$] (R = *p*-C$_6$H$_4$CF$_3$, ^{n}Bu) have been prepared for the first time, and studied alongside precedent analogues (R = Me, Ph, *p*-tol) for their reactions with HCl. In contrast to chemistry defined for the *tert*-butyl congener [Ru{P=C(H)^{t}Bu}Cl(CO)(PPh$_3$)$_2$], which initially adds a single equivalent of HCl across the Ru-P linkage, all five silyl derivatives undergo spontaneous addition of a second equivalent to afford [Ru{η^1-PHCl–CH$_2$SiMe$_2$R}Cl(CO)(PPh$_3$)$_2$], extremely rare examples of coordinated 'PHXR' type ligands. Where R = SiMe$_3$, a distorted octahedral geometry with a conformationally restricted 'PHXR' ligand is observed crystallographically; this structure is appreciably retained in solution, as determined from multinuclear NMR spectroscopic features, which include a Karplus-like P_{PPh3}–Ru–P–H spin-spin coupling dependence. Computational data suggest a silyl-induced increase in negative charge density at the phosphaalkenic carbon, rather than an intrinsic thermodynamic driver, as the likely origin of the disparate reactivity.

INTRODUCTION

Phosphaalkenes were among the earliest examples of phosphacarbon to be isolated[1] and have thus been extensively investigated for their chemistry.[2] Due to the very modest polarization of the P=C linkage ($P^{\delta+}$=$C^{\delta-}$), facile control of their reactivity can be achieved via substituent modification, to which end a wide range of derivatives is known. Still, sterically unencumbered phosphaalkenes (e.g. HP=CHR), which lack kinetic stability, remain unisolated.[3,4]

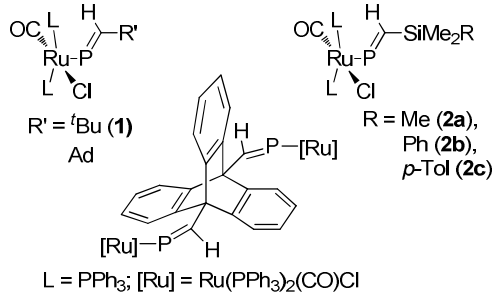
In seeking to impart stability, and indeed direct reactivity, transition metal fragments have proven to be particularly versatile tools, with a wide variety of η^1, and to a lesser extent η^2, phosphaalkene complexes having been studied.[5] Moreover, the direct incorporation of transition metal (or main group element) fragments as substituents on the 'P=C' core (**A – E**; Chart 1) has received significant attention,[6] with examples of all possible metallaphosphaalkene motifs (with the exception of type **E**) having been described. The overwhelming focus, however, has been on *P*-metalla- (type **A**) and *C*-metalla- (type **B**) systems, which offer direct analogy to classical organometallic alkenyl complexes. Intriguingly, in the case of *P*-metallaphosphaalkenyls, scope also exists for involvement of the lone-pair in metal-ligand binding, with several instances of phosphavinylidene (M=P=CR$_2$) character being noted.[7]

Chart 1: Metallaphosphaalkenyl motifs



While a variety of synthetic routes have been used to access compounds of type **A**,[8-13] among the most facile is the stoichiometric reduction of phosphaalkynes by a transition metal hydride. This was first demonstrated by Hill and Jones in 1996,[14] hydroruthenation of ^{t}BuC≡P with [RuHCl(CO)(PPh$_3$)$_3$] affording [Ru{P=C(H)^{t}Bu}Cl(CO)(PPh$_3$)$_2$] (**1**), in analogous fashion to the synthesis of classical ruthenium vinyls from alkynes.[15] A handful of further examples have followed (Chart 2),[16-18] while Nixon independently described hydrozirconation of the π-bound phosphaalkyne in [Pt(η^2-P≡C^{t}Bu)(PPh$_3$)$_2$] using Schwartz's reagent.[19]

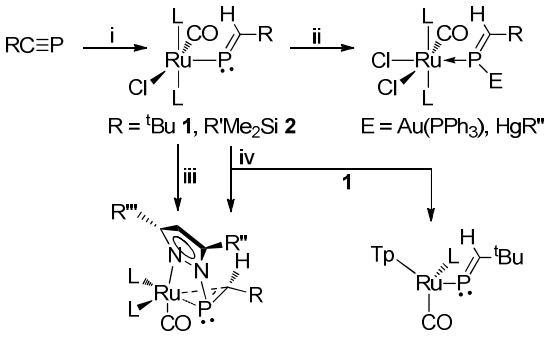
Chart 2: Known *P*-Ruthenaphosphaalkenyls[14,16-18]



Recently, we have applied Hill's hydroruthenation protocol to the synthesis of a range of silyl-substituted phosphaalkenyls, derived from RMe$_2$SiC≡P (R = Me **2a**, Ph **2b**, *p*-Tol **2c**),[18] providing also the first structural data for such compounds.[18a] Taken alongside computational (DFT) data, this unequivocally demonstrated the absence of any phosphavinylidene character in the ground state structures, corroborating Hill's formulation of the phosphacarbon in **1** as a discrete 1-electron phosphaalkenyl moiety.[20] This formulation is consistent with observed nucleophilicity of the phos-

phorus centers in **1** and **2a**, which undergo addition of electrophilic fragments upon their reaction with R'X, to afford the η^1-phosphaalkene complexes [Ru{η^1-P(R')=C(H)R}ClX(CO)(PPh_3)$_2$] (R = tBu, $SiMe_3$).[18b,20] Notwithstanding, we have observed apparent ambiphilicity for this center,[18] which is seemingly functionalized just as readily by nucleophilic fragments, reactions with pyrazolate anions ([pz']$^-$) affording the intramolecularly chelated η^2-pyrazolylphosphaalkene complexes [Ru{η^1-N:η^2-P,C-P(pz')=CHR}(CO)(PPh_3)$_2$] (Scheme 1). Moreover, the latter also form serendipitously upon reaction of **2a–c** with KTp', in contrast to the analogous reaction of **1** (where Tp' = Tp), which affords the expected [TpRu(P=C(H)^{t}Bu)(CO)(PPh_3)].[16,21] This would seem to imply an appreciable influence of the nature of the phosphaalkenyl '*C*'-substituent upon reactivity at the metal and/or Ru-P linkage.

Scheme 1: Representative synthesis and reactivity of ruthenaphosphaalkenyls.



Reagents and conditions: i) CH_2Cl_2, [RuHCl(CO)(PPh_3)$_3$], 1h.; ii) ECl, CH_2Cl_2, 1h.; iii) Lipz', thf, 1h.; iv) KTp', CH_2Cl_2, 1h.

Intrigued by this behavior, we have sought to further investigate the chemistry of the ruthenaphosphaalkenyls, with a particular focus on exploring the influence exerted by subtle variation in the terminal alkenyl substituent. To this end, we report herein the synthesis of further novel examples of ruthenaphosphaalkenyls and the unexpectedly non-trivial interactions of such compounds with HCl, affording facile access to, very rare, alkylchlorohydrophosphane complexes.

RESULTS AND DISCUSSION

Ruthenaphosphaalkenyls **2a–c** were prepared as previously described,[18] and the novel analogues [Ru{P=C(H)$SiMe_2$R}-Cl(CO)(PPh_3)$_2$] (R = *p*-$C_6H_4CF_3$ **2d**, ^{n}Bu **2e**) obtained in similar fashion, *viz.* hydroruthenation by [RuHCl(CO)(PPh_3)$_3$] of the novel phosphaalkynes R$Me_2SiC{\equiv}P$ (R = *p*-$C_6H_4CF_3$, ^{n}Bu). Both **2d** and **2e** exhibit the characteristic spectroscopic features previously established for **2a–c**, indicative of the phosphaalkenyl (δ_P 559.7, δ_H 7.32 **2d**; δ_P 545.3, δ_H 7.32 **2e**) and PPh_3 (δ_P 33.8) moieties, and the retention of a ruthenium(II) center (ν_{CO} 1939 cm^{-1} **2d**, 1930 cm^{-1} **2e**); signatures for the ancillary organic groups are also observed, while the bulk purity is confirmed by microanalytical data.

It is noteworthy that the phosphorus and carbon centers (Table 1) exhibit shielding trends consistent with those defined for vinyl- and aryl silanes.[22] Thus, increased alkyl substitution at silicon (**2a**, **e**) leads to deshielding of the α-center (C), while the β (phosphorus) center becomes more shielded. Moreover, as we have previously noted,[18a] on replacing silicon with carbon (i.e. ^{t}Bu derivative **1**) these effects are greatly enhanced, implying significantly reduced σ-density at the α-carbon center, while phosphorus becomes heavily shielded. One might thus anticipate disparate reactivity between **1** and **2**, although this has not, thus far, been observed.

Table 1: Key NMR spectroscopic features for the ruthenaphosphaalkenyls 1 and 2a-e.

	1[a]	2a[a]	2b[a]	2c[b]	2d[b]	2e[b]
δ_P	450.4	548.5	553.8	552.6	559.7	545.3
δ_C	184.9	168.0	163.7	165.2	162.9	165.9

[a]$CDCl_3$ solution; [b]CD_2Cl_2 solution.

The addition of electrophilic reagents across the Ru–P linkage of ruthenaphosphaalkenyls has been well-established,[18,20] and includes in the case of **1** hydrochlorination to afford [Ru(η^1-PH=CH^{t}Bu)Cl_2(CO)(PPh_3)$_2$] (**3**).[20c] Given the typically analogous behavior of the silylated derivatives (e.g. in the addition of PhHgCl[18b]), we envisaged the trivial extension of this hydrochlorination reaction to such systems; thus, each of **2a-e** was treated with a stoichiometric amount of HCl in ether. However, after removal of the volatiles, the $^{31}P\{^1H\}$-NMR spectra indicated in each case retention of the phosphaalkenyl complex as a 1:1 mixture with a new species (**4a-e**). The latter is obtained exclusively when at least 2-fold excess of HCl is used, while sub-stoichiometric amounts yield statistical mixtures with the parent (**2a-e**).

Compounds **4a-e** each exhibit distinctive $^{31}P\{^1H\}$ NMR spectra, based on an ABB' spin system (Figure 1 and SI) arising from the phosphacarbon (δ_P ~ 80) and now inequivalent PPh_3 (δ_P ~ 26, 22) fragments, all of which are appreciably shielded from those of the parent phosphaalkenyls. This is

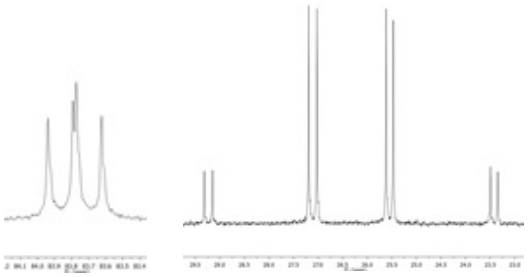


Figure 1: Phosphacarbon (left) and PPh_3 (right) $^{31}P\{^1H\}$ NMR resonances of the ABB' spin system of **4b**.

particularly notable for the phosphacarbon resonance ($\Delta\delta_P$ ~ –460), which is now more consistent with a phosphane functionality. Indeed, heteronuclear correlation experiments (^1H-^{13}C, ^1H-^{31}P, ^1H-^{29}Si) demonstrate saturation of the adjacent carbon center to CH_2SiMe_2R, the diasterotopic methylene protons each exhibiting a distinct $^2J_{PH}$ coupling (~15 Hz), which is also reflected in the ^{31}P-NMR spectra as a higher-order pattern for the phosphacarbon resonance. A $^1J_{PH}$ scalar interaction (438 Hz) is also manifest, the multiplicity and integration of the associated proton resonance (δ_H ~ 5.27) confirming a 'PH' moiety. Given also the apparent retention of a ruthenium(II) center (ν_{CO} ~ 1970 cm^{-1}) and relatively deshielded nature of the phosphane resonance, we conclude these data to be consistent with the formulation [Ru(P(H)ClCH_2-$SiMe_2$R)Cl_2(CO)(PPh_3)$_2$] (**4**). The bulk composition data are consistent with this notion, which was ulti-

mately confirmed in the case of **4a** by a single crystal X-ray diffraction study (Figure 2).

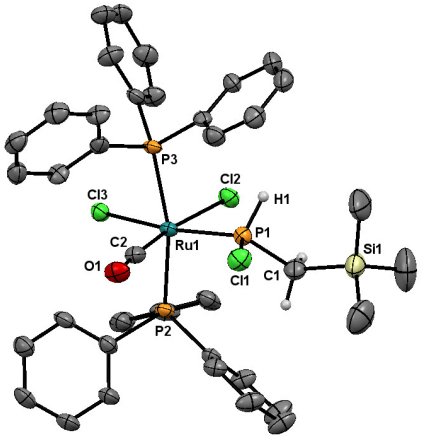


Figure 2: Molecular structure of **4a** in crystals of the CH_2Cl_2 solvate; 50 % thermal ellipsoids, ancillary hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Ru–P1 2.281(2), Ru–P2 2.402(2), Ru–P3 2.419(2), Ru–Cl2 2.469(2), Ru–Cl3 2.447(2), Ru–C2 1.850(9), C2–O1 1.146(10), P1–C1 1.790(11), P1–Cl1 2.059(3), C1–Si1 1.914(10); P2–Ru–P3 166.50(7), C2–Ru–Cl2 168.0(3), C2–Ru–Cl3 100.7(3), C2–Ru–P1 88.9(3), P1–Ru–Cl2 76.21(7), Cl2–Ru–Cl3 91.33(6), Ru–P1–C1 125.2(3), Ru–P1–Cl1 115.67(10), P1–C1–Si1 118.0(6).

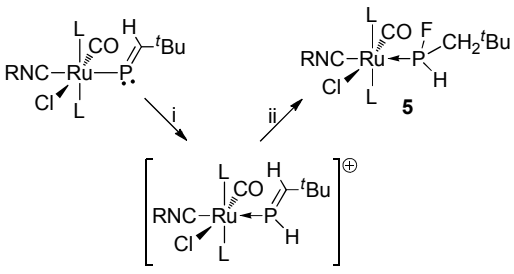
The core geometry of **4a** is distorted octahedral with *cis* interligand angles in the range 76.21(7) – 100.7(3) °, while the *trans* Cl–Ru–CO (168.0(3) °) and Ph_3P–Ru–PPh_3 (166.50(7) °) arrangements are appreciably non-linear. In the latter case, this can be attributed to the steric demand of the phosphacarbon moiety, which is significantly displaced from the equatorial plane ($\phi_{(Cl\text{-}Ru\text{-}P\text{-}C)}$ = 56.3(4) °) in contrast to the coplanar arrangement observed for the closest structural comparator, *viz.* [Ru(P(H)FCH_2^{t}Bu)Cl(CNXyl)(CO)(PPh_3)$_2$] (**5**).[20a] The phosphacarbon fragments of the two complexes, however, are largely comparable, exhibiting relatively short Ru–P (2.281(2) **4a**; 2.352(2) Å **5**) and P–C (1.790(11) **4a**; 1.794(6) Å **5**) linkages, with appreciable opening of the bond angles (Ru–P–C 125.2(3) ° **4a**, 120.1(2) ° **5**; P–C–Si 118.0(6)° **4a**, P–C–C 121.1(5) ° **5**). Such features are common among the very limited range of structurally characterized complexes featuring a PX_2R or PXHR ligand,[23,24] and have been taken to imply an enhanced π-acidity for the phosphane fragment;[20a] indeed, this would seem consistent with the appreciable increase observed in ν_{CO} ($\Delta\nu$ ~ +50 cm^{-1}) for **4a-e** in comparison to the parent phosphaalkenyls, which implies significant reduction of electron density at the metal.

The conformational arrangement of the phosphacarbon moiety with respect to the molecular plane of **4a–e** is noteworthy, and is apparently retained in solution. In each case, the ^{31}P-^1H HMBC spectra demonstrate a significant spin-spin interaction between 'PH' hydrogen and the phosphorus center of one PPh_3 ligand, with a much lower magnitude coupling to its counterpart. Most likely arising from a $^3J_{PH}$ bond-mediated pathway, this coupling would appear consistent with a Karplus-like[25-28] torsional dependence (P–H vs Ru–P vectors). Indeed, such behavior has been previously defined for P–Ru–S–H systems, with maximum and minimum coupling magnitudes observed at ϕ ~ 180 ° and 90 ° respectively,[29] against which structural data for **4a** (ϕ = 152.1, −31.5 °) may be compared.

Though partial rotation of the phosphaalkyl moiety in **4a-e** cannot be excluded for the solution phase (indeed, a rigid structure would seem unlikely), couplings of such disparate magnitude requires this to be appreciably restricted, to allow adequate evolution time. This would, however, appear to contrast the situation for **5**, in which the intrinsically diastereotopic PPh_3 ligands appear as equivalent on the NMR timescale. Given that for **5** coupling between the 'PFHR' and PPh_3 moieties was still resolved (J_{PP} 31 Hz) and that the reported $\delta_{P(PPh3)}$ (24.4)[20a] is comparable to those of **4** (δ_P 26, 22) a dissociative dynamic exchange of PPh_3 can be excluded.[30] It would thus seem that the PPh_3 ligands of **5** experience (under proton decoupling at least) a locally pseudo-achiral magnetic environment, the origin of which is not immediately apparent. Indeed, the only substantive distinctions between **4** and **5** lie with the reduced steric footprint of 'PFHR' (*cf.* 'PClHR'), and its somewhat weaker binding, presumably the result of reduced metal→ligand π-donation in the presence of a competing *trans*-π-acid (CNXyl). While such might reasonably lead to rotation about the Ru–PFHR linkage being more facile, the apparent loss of chirality under fast-exchange would seem unlikely. Thus, in lieu of specific further study of **5**, we are presently unable to comment.

The formation of **4a-e** is superficially reminiscent of the generation of **5** via sequential treatment of the coordinately saturated [Ru(P=CH^{t}Bu)Cl(CO)(CNXyl)(PPh_3)$_2$] with HBF_4 and K[HF_2] (Scheme 2).[20a] By analogy, an intermediate of the type [Ru(η^1-PH=CHSiMe_2R)Cl_2(CO)(PPh_3)$_2$] (**A**) might reasonably be invoked, albeit unobserved. Indeed, this would be consistent with the reported product of HCl addition to **1**, *viz.* [Ru(η^1-PH=CH^{t}Bu)Cl_2(CO)(PPh_3)$_2$] (**3**),[20c] albeit that no further reaction of **3** was described. Intrigued by this disparity, we re-examined the reactivity of **1** on an analytical (NMR) scale. Thus, the stoichiometric, or sub-stoichiometric, treatment of a CD_2Cl_2 solution of **1** with ethereal HCl effects proportional conversion to a single species that is spectroscopically comparable to **3**[20c] ($\delta_{P(PH=C)}$ 189.0; $\delta_{P(PPh3)}$ 16.7, J_{PP} 40 Hz; $\delta_{H(PH)}$ 5.38, J_{PH} 376 Hz), these data also being consistent with those obtained from other additions across the Ru–P linkage. However, upon treatment with excess of HCl, this spectroscopic signature is lost, with formation of a new species (**6**), the resonances of which are comparable to those observed for **4a-e**, *viz.* δ_P 75.5 (J_{PP} 27, 25 Hz), 25.4 (J_{PP} 347, 27 Hz), 21.8 (J_{PP} 347, 25 Hz), and thus seemingly consistent with formation of [Ru(P(H)ClCH_2^{t}Bu)Cl_2(CO)(PPh_3)$_2$].

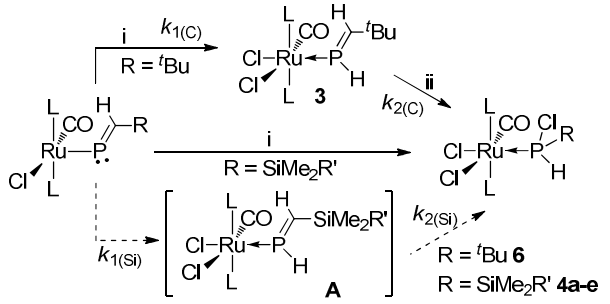
Scheme 2. Synthesis of complex 5.[20a]



Reagents conditions .i) $HBF_4.OEt_2$; ii) K[HF_2]. L = PPh_3, R = $C_6H_3Me_2$-2,6.

These experimental observations would appear consistent with both **1** and **2** undergoing similar sequential additions of the two HCl equivalents. For the silyl derivatives (**2**), the second addition step is more facile (i.e. $k_{2(Si)} >> k_{1(Si)}$, Scheme 3), such that formation of **A** is followed by its rapid conversion to **4**, precluding observation or interception. In contrast, for **1**, $k_{1(C)} >> k_{2(C)}$, thus formation of **3** proceeds to completion before any subsequent conversion to **6**. Preliminary computational studies (see Supporting Information)[31] would seem to preclude a thermodynamic origin for this discrimination, both **A** and **3** being ca 17 kcal mol^{-1} more stable than their precursors, a situation that is mirrored by **4** and **6** (ca 33 kcal mol^{-1} more stable).

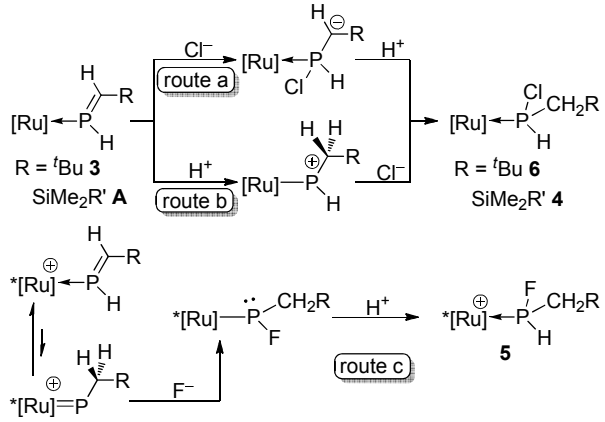
Scheme 3. Formation of complexes 4 and 6.



Reagents and conditions: i) 1 equiv. HCl.OEt$_2$, ii) xs HCl.OEt$_2$

In considering the specifics of the reaction one can reasonably suggest this second addition process to occur in a stepwise fashion (Scheme 4), proceeding *either* by halide attack at an intrinsically electrophilic phosphorus center (route a), *or* by protonation of the β-carbon (route b). It is noteworthy that in respect of the formation of **5**, Hill suggested also a third alternative,[20a] based on proton-shuttling between phosphorus and the β-carbon, giving rise to a transient phosphinidene (route c); nonetheless, this also equates to a β-protonation step (albeit intramolecular), thus again requiring appreciable nucleophilicity at this site.

Scheme 4. Possible mechanisms for HCl addition to η^1-phosphaalkene complexes.



*[Ru] = RuCO(PPh$_3$)$_2$Cl$_2$; *[Ru] = RuCO(CNXyl)(PPh$_3$)$_2$Cl*[20a]

In this context, NBO calculations performed on **A** and **3** offer a qualitative insight. These illustrate the anticipated polarization of the phosphaalkene moieties (*viz.* P$^{\delta+}$=C$^{\delta-}$) with significant, and comparable, positive charge density at phosphorus (0.99 **A**, 0.93 **3**). However, the silyl derivative **A** exhibits notably greater build-up of negative charge density at the β-carbon (−1.12) than does **5** (−0.59), implying (on an electrostatic basis at least) a significantly more nucleophilic site. If the addition of HCl follows either route b or c, this offers a feasible source of discrimination between the two systems, such that protonation of **A** should be appreciably more facile than that of **3** (*i.e.* $k_{2(Si)} >> k_{2(C)}$), thus presenting a lower kinetic barrier for the conversion **A→4** than that for **3→6**. In contrast, no such discrimination would follow from route a, which might reasonably be dismissed. However, in lieu of observing species **A**, this cannot be verified, nor can one assess the relative facility of the two HCl addition processes (i.e. k_1 vs k_2) without knowledge of the intimate mechanism for each step. This also precluded distinction between routes b and c. A definitive reaction pathway thus remains to be determined, but is the subject of on-going investigations.

Regardless of the mechanistic features, and indeed the disparate reactivity observed, the formation of complexes **4a-e** is in itself remarkable, not least in being a still rare example of the complete reduction of phosphaalkynes within a metal coordination sphere. Moreover, phosphanes of the type PH(X)R (particularly where R = alkyl) are intrinsically unstable toward HX elimination, oligomierization and disproportionation to RPH$_2$ / RPX$_2$. Thus, few have been discretely observed,[32] with a mere handful generated within metal coordination spheres,[24,33] though typically via non-trivial methodology. This report thus offers truly facile access to an intriguing range of compounds, with significant potential for further chemistry.

CONCLUDING REMARKS

Extending our investigations of ruthenaphosphaalkenyl complexes, derived by hydroruthenation of the phosphaalkynes RMe$_2$SiC≡P, we have explored the reactions of [Ru{P=C(H)SiMe$_2$R}Cl(CO)(PPh$_3$)$_2$] (R = Me, Ph, *p*-Tol, *p*-C$_6$H$_4$CF$_3$, ^{n}Bu) toward HCl. These afford exclusively the complexes [Ru(P(H)ClCH$_2$SiMe$_2$R)Cl$_2$(CO)(PPh$_3$)$_2$], and thus constitute facile access to the very rare alkylchlorohydrophosphane ligands. A structural preference for co-alignment of the P–Cl and CO moieties is apparent from solid state (x-ray) and solution data, the latter indicating magnetic inequivalence of the ancillary PPh$_3$ ligands, which exhibit $^3J_{PH}$ coupling interactions with the phosphane 'PH' unit, the relative magnitudes of which are consistent with a Karplus-like torsional dependence.

The observed reactivity contrasts that of [Ru{P=C(H)^{t}Bu}-Cl(CO)(PPh$_3$)$_2$], which reacts with HCl to afford initially [Ru(η^1-PH=CH^{t}Bu)Cl$_2$(CO)(PPh$_3$)$_2$], further reaction proceeding only in the presence of excess acid. This disparity, would appear to be kinetic, rather than thermodynamic in origin, and might reasonably be attributed to the relative influence of the β-substituents (silyl vs tert-butyl) within the intermediate η^1-phosphaalkene complex. Thus, on the basis of computational data, one can invoke enhanced negative charge density at the β-carbon of the silyl derivatives, leading to a reduced kinetic barrier for rate limiting protonation at this site. Notwithstanding, the intimate mechanism remains to be established, and is the subject of continuing investigations.

Irrespective of the mechanistic minutiae, this reaction represents facile access to complexes of the incredibly rare hydrochlorophosphane ligands. Featuring an intrinsically chiral ligand bearing a reactive halide substituent, such com-

plexes offer considerable interest in terms of the chemistry, including potential for further ligand development, which we are presently investigating.

EXPERIMENTAL SECTION

General Methods. All manipulations were performed under strict anaerobic conditions using standard Schlenk line and glovebox (MBraun) techniques, working under an atmosphere of dry argon or dinitrogen respectively. Solvents were distilled from appropriate drying agents and stored over either molecular sieves (4 Å, for DCM and THF) or potassium mirrors. General reagents were obtained from Sigma-Aldrich or Fisher and purified by appropriate methods before use, precious metal salts were obtained from STREM. RMe_2SiCH_2Cl (R = C_6F_5,[34] ^{n}Bu[35]), $RMe_2SiCH_2PCl_2$ (R = Me,[36] Ph,[36] Tol,[18a]), ^{t}BuC≡P,[37] $Me_3SiC{=}P$[18,38] [RuHCl(CO)(PPh_3)$_3$],[39] and [Ru{P=CH(^{t}Bu)}Cl(CO)(PPh_3)$_2$] (R = ^{t}Bu[14,16], $SiMe_3$, $SiMe_2Ph$, $SiMe_2$Tol[18]) were prepared as previously described. Unless otherwise stated NMR spectra were recorded at 303 K, on Varian VNMRS 400 (^{1}H 399.50 MHz, ^{13}C 100.46 MHz, ^{19}F 375.87 MHz, ^{31}P 161.71 MHz, ^{29}Si 79.37 MHz); VNMRS 500 (^{1}H 499.91 MHz, ^{13}C 125.72 MHz) or 600 (^{1}H 599.69 MHz, ^{13}C 150.81 MHz, ^{31}P 242.83 MHz) spectrometers were used in selected instances. All spectra are referenced to external Me_4Si, 85 % H_3PO_4 and $CFCl_3$ as appropriate. Carbon-13 spectra were assigned by recourse to the 2D (HSQC, HMBC) spectra; phosphaalkenic proton and silicon shifts were determined indirectly by ^{1}H-^{31}P and ^{1}H-^{29}Si correlation (HMBC). Elemental analyses (performed by Mr S. Boyer of the London Metropolitan University Elemental Analysis Service) were obtained on samples taken from the bulk material yielded by the final purification step indicated in the experimental text.

X-ray diffraction studies. Single crystal X-ray diffraction data were recorded on an Agilent Xcalibur Eos Gemini Ultra diffractometer with CCD plate detector using Cu-Kα (λ = 1.54184 Å) radiation. Structure solution and refinement were performed using SHELXS[40] and SHELXL[40] respectively, running under Olex2.[41]

DFT calculations. Calculations were performed using Gaussian 09W, Revision C.01,[42] running on an Intel Core i5-2500 (quad, 3.3 GHz), equipped with 4 GB RAM; results were visualized using GaussView 5.0. Geometries were optimized with the hybrid density functional B3LYP, using the RECP basis set Lanl2dz for Ru and 6-31G** for all other atoms. Minima were characterized by frequency calculations at the same level of theory. Single point energy calculations were subsequently performed with the B3LYP functional, using Lanl2dz for Ru and the 6-311+G** basis set for all other atoms. NBO calculations were performed at the same level of theory.

(*p*-$CF_3C_6H_4$)$Me_2SiCH_2PCl_2$. In a modification of literature methods for related compounds,[25,18a] (*p*-$CF_3C_6H_4$)Me_2SiCH_2Cl[34] (4.8 g, 0.019 mol) in ether (50 cm^3) was added, drop-wise, to a stirring suspension of activated Mg (0.8 g, 0.032 mol) in ether (50 cm^3). The mixture was heated to reflux for 5 h. After allowing to cool to ambient temperature the solution was filtered directly into a cold (−78 °C) ethereal solution (20 cm^3) of PCl_3 (1.7 cm^3, 0.019 mol). The mixture was then stirred for 1 h. at this temperature, before being allowed to warm to ambient temperature over the course of 18 h. The solution was filtered and the residues washed with Et_2O (3 x 15 cm^3); the combined filtrate was stripped of Et_2O by distillation at ambient temperature to afford a yellow liquid, which was distilled to purity at low pressure (55 °C, 5.0 x 10^{-2} mbar). Yield: 3.52 g, 58 %. ^{1}H NMR ($CDCl_3$): δ_H 0.51 (d, $^4J_{PH}$ 1 Hz, 6H, $SiMe_2$), 2.24 (d, $^2J_{PH}$ = 15.6 Hz, 2H, CH_2), 7.63 (m, 4H, Ar-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ_C -1.5 (d, $^3J_{PC}$ 4 Hz, $SiMe_2$), 34.5 (d, $^1J_{C\text{-}P}$ = 62 Hz, CH_2P), 124.8 (q, $^1J_{CF}$ 4 Hz, Ar-C), remaining resonances unresolved. ^{19}F-NMR ($CDCl_3$): δ_F −63.13 (s, CF_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P 200.8.. ^{29}Si NMR ($CDCl_3$): δ_{Si} -4.6. Anal Found: C, 37.75 %; H, 3.84 %. Calcd for $C_{10}H_{12}Cl_2F_3PSi$: C, 37.65 %; H, 3.79 %.

***n*-$BuMe_2SiCH_2PCl_2$.** Following literature precedent for related materials,[18a] *n*-$BuMe_2SiCH_2Cl$[35] (5.0 g, 0.030 mol) in ether (15 cm^3) was added, drop-wise, to a stirring suspension of activated Mg (2.0 g, 0.08 mol) in ether (20 cm^3), at a rate to maintain reflux. Stirring was continued while the reaction cooled to ambient temperature, and then for a further 2 h.; the mixture was then filtered directly into an ethereal solution (20 cm^3) of PCl_3 (2.7 cm^3, 0.030 mol) held at −78 °C. The mixture was then stirred for 30 minutes at this temperature, before being allowed to warm to ambient temperature over the course of 18 h. The solution was filtered and the residues washed with Et_2O (3 x 15 cm^3); the combined filtrate was stripped of Et_2O by distillation at ambient temperature to afford a colorless liquid. The crude material was resistant to distillation, but adequately pure (95 % by ^{31}P NMR integration) to utilize in phosphaalkyne synthesis. Yield (crude): 6.4 g, 90 %. ^{1}H NMR ($CDCl_3$): δ_H 0.18 (s, 6H, $SiMe_2$), 0.68 (m, 2H, $SiCH_2$), 0.90 (t, J_{HH} 6.8 Hz, 3H, CH_2CH_3), 1.33 (m, 4H, 2 x CH_2), 2.03 (d, $^2J_{PH}$ = 15.4 Hz, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ_C -1.6 (d, $^3J_{PC}$ 6 Hz, $SiMe_2$), 13.8 (s, $CH_2\underline{C}H_3$), 25.9 (s, 2 x CH_2), 26.5 (s, Si-$\underline{C}H_2$), 34.5 (d, $^1J_{C\text{-}P}$ = 62 Hz, CH_2P). ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P 205.6.. ^{29}Si NMR ($CDCl_3$): δ_{Si} 1.2.

$RMe_2SiC{\equiv}P$ (R = $C_6H_4CF_3$-*p*, *n*-Bu). As we have previously described for R = Me, Ph, Tol,[18,38] $RMe_2SiCH_2PCl_2$ (2.4 mmol) as solution in toluene was added to a toluene suspension of AgOTf (1.26 g, 4.9 mmol); after stirring for 10 min., DABCO (0.550 g, 4.9 mmol) was added as solution toluene. After stirring for 1 h. the mixture was filtered and then calibrated for concentration by integration of its ^{31}P{^{1}H}-NMR resonance (δ_P 106.7 **$C_6H_4CF_3$**; 101.2 ***n*-Bu**) against that of fully relaxed (d_1 = 150 s) PPh_3. The stock solutions were stored below 5 °C (< 1 week) and recalibrated prior to use.

[Ru{P=CH($SiMe_2$R)}Cl(CO)(PPh_3)$_2$] (R = $C_6H_4CF_3$-*p* 2d, *n*-Bu 2e). As previously described for **2a-c**.[18] In a typical reaction, to a stirring suspension of [RuHCl(CO)(PPh_3)$_3$] (1.5 g, 1.53 mmol) in CH_2Cl_2 (15 cm^3) was added an excess (1.3 equiv.) of $RMe_2SiC{\equiv}P$ as solution in toluene (ca 25 cm^3). After stirring for 1 h. the solvent was removed under reduced pressure to afford an orange/brown residue, which was washed vigorously with *n*-hexane (3 x 10 cm^3). The solvent was then removed by filtration, to afford a yellow to orange solid, which was dried *in vacuo*. **Data for 2d:** Yield: 75 %. ^{1}H-NMR (CD_2Cl_2, 499.9 MHz): δ_H 0.27 (s, 6H, $SiMe_2$), 7.34 − 7.38 (m, 12 H, Ar), 7.32 (br. s, 1H, P=C**H**), 7.42 – 7.48 (m, 10H, Ar), 7.55 – 7.60 (m, 12 H, Ar). ^{13}C{^{1}H}-NMR (CD_2Cl_2) δ_C −0.9 (*d*, J_{CP} 7.6 Hz, Si($\underline{C}H_3$)$_2$), 124.5 (q, J_{FC} 3.7 Hz, C, $\underline{C}$-CF_3), 125.1 (q, J_{FC} 272 Hz, *C,* CF_3), 128.8 (t, J_{PC} 5.1 Hz, *CH*, PAr), 129.1 (s, CH, C_6H_4), 131.0 (s, CH, PAr), 131.1 (s, CH, C_6H_4), 132.6 (t, J_{PC} 22.9 Hz, C, PAr), 134.9 (t, J_{PC} 5.8 Hz, CH, PAr), 162.7 (dt, J_{PC} 162.3, 2.7 Hz, CH, P=*C*H), 202.4 (t, J_{PC} 14.5 Hz, C≡O). ^{31}P{^{1}H}-NMR (CD_2Cl_2) δ_P 33.8 (*d*, J_{PP} 8.3 Hz, PPh_3), 559.7 (*t*, J_{PP} 8.3 Hz, P=C). ^{19}F NMR ($CDCl_3$): δ_F −63.13 (s, CF_3). ^{29}Si{^{1}H}-NMR (CD_2Cl_2) δ_{Si} −14.0. ν_{CO} = 1939 cm^{-1}. Anal. Found: C, 60.45; H, 4.57; Calcd for $C_{47}H_{41}ClF_3OP_3RuSi$: C, 60.30; H, 4.41.

Data for 2e: Yield: 82 %. ^{1}H-NMR (CD_2Cl_2, 499.9 MHz): ^{1}H-NMR (CD_2Cl_2, 499.9 MHz): δ_H −0.05 (s, 6H, $SiMe_2$), 0.47 (m, 2H, $SiCH_2$), 0.82 (*t*, *J* 7.1 Hz, 3H, CH_3), 1.16 (m, 2H, CH_2), 1.25 (m, 2H, CH_2), 7.10 − 7.46 (m, 20 H, Ar), 7.32 (br. s, 1H, P=C**H**), 7.59 – 7.64 (m, 10 H, Ar). ^{13}C{^{1}H}-NMR (CD_2Cl_2) δ_C −0.8 (*d*, J_{PC} 7.5 Hz, Si($\underline{C}H_3$)$_2$), 14.2 (s, CH_3), 17.4 (d, J_{PC} 5.3 Hz, $SiCH_2$), 26.7 (s, CH_2), 27.1 (s, CH_2), 128.8 (t, J_{PC} 5.1 Hz, Ar), 130.9 (s Ar), 132.8 (t, J_{PC} 23 Hz, Ar), 135.0 (t, J_{PC} 5.6 Hz, Ar), 166.6 (dt. $^1J_{PC}$ 76 Hz, $^3J_{PC}$ 3 Hz, CH, P=*C*H), 202.8 (d, J_{PC} 14.5 Hz, C≡O). ^{31}P{^{1}H}-NMR (CD_2Cl_2) δ_P 33.8 (*d*, J_{PP} 8.3 Hz, PPh_3), 545.3 (*t*, J_{PP} 8.3 Hz, P=C). ^{29}Si{^{1}H}-NMR (CD_2Cl_2) δ_{Si} −7.3. ν_{CO} = 1930 cm^{-1}. Anal. Found: C, 62.19; H, 5.39; Calcd for $C_{44}H_{46}ClOP_3RuSi$: C, 62.30; H, 5.47.

[Ru(P(H)ClCH$_2$SiMe$_3$)Cl$_2$(CO)(PPh$_3$)$_2$] (4a). In a typical preparative reaction, to a stirred solution of **2a** (0.30 g, 3.72 x 10^{-4} mol) in dichloromethane (ca 5 cm^3) was added excess of anhydrous HCl as solution in Et_2O (1 cm^3, 1 M, 10 x 10^{-4} mol), resulting in immediate decolorization. The volatiles were removed under reduced pressure, the product washed with Et_2O and hexanes, then dried *in vacuo* to afford a pale yellow solid. Yield: 0.285 g, 87 % (isolated). ^{1}H-NMR: δ_H −0.25 (s, 9H, $SiMe_3$), −0.06 (dm, 1 H, J_{PH} 26.1 Hz, PCH_2), 1.41 (dm, 1H, J_{PH} 14.8 Hz, PCH_2), 5.27 (dtd, 1H, J_{PH} 424.5 Hz, J_{HH} 2,

10.8 Hz, PH), 7.29 – 7.43 (m, 18 H, Ar), 7.76 – 7.87 (m, 6H, Ar), 7.89 – 7.98 (m, 6 H, Ar). $^{13}C\{^1H\}$-NMR: δ_C –0.82 (s $SiMe_3$), 17.1 (d, J_{PC} 20 Hz, P<u>C</u>H_2), 128.1 (m, Ar), 130.2 (s, Ar), 131.6 (*dd*, J_{PC} 38.6, 5 Hz, C, Ar), 135.3 (t, J_{PC} 8.5 Hz, CH, Ar), 199.3 (*m*, C≡O), $^{31}P\{^1H\}$-NMR : δ_P 22.4 (*dd*, J_{PP} 23.8, 343 Hz PPh_3), 26.5 (*dd*, J_{PP} 27.8, 343 Hz, PPh_3), 84.2 (*dd*, J_{PP} 23.8, 27.8 Hz, P=C). $^{29}Si\{^1H\}$-NMR: δ_{Si} 3.43. ν_{CO} = 1970 cm^{-1}. Anal. Found: C, 55.98; H, 4.73; Calcd for $C_{41}H_{42}Cl_3OP_3RuSi$: C, 56.02; H, 4.81.

$C_{41}H_{42}Cl_3OP_3RuSi.CH_2Cl_2$, M_w = 964.09, triclinic, P -1 (no. 2), a = 12.5318(8), b = 13.0932(11), c = 15.9653(10) Å, α = 99.390(6), β = 101.138(5), γ= 116.048(7) °, V = 2215.9(3) $Å^3$, Z = 2, D_c = 1.445 Mg m^{-3}, μ(Cu-Kα) = 7.168 mm^{-1}, T = 173(2) K, 8091 independent reflections, full-matrix F^2 refinement R_1 = 0.0754, wR_2 = 0.2295 on 6095 independent absorption corrected reflections [I > 2σ(I); 2θ_{max} = 142.3 º], 494 parameters, CCDC 1510476

[Ru(P(H)ClCH$_2$SiMe$_2$R)Cl$_2$(CO)(PPh$_3$)$_2$] (4b-e). Reactions were performed on an analytical scale, using ca 20 mg of **2b-e** dissolved in CD_2Cl_2 in an NMR tube, with ca 0.1 cm^3 HCl/Et_2O. Crude NMR spectroscopic data imply quantitative conversion to **4b-e**. After removal of volatiles and redissolution, full spectroscopic data were obtained; the samples were then dried *in vacuo* to allow for bulk compositional analysis.

4b (R = Ph): ^1H-NMR (CD_2Cl_2): δ_H 0.01 (s, 3H, $SiMe_2$), 0.04 (s, 3H, $SiMe_2$), 0.15 (dm, 1 H, J_{PH} 25.7 Hz, PCH_2), 1.41 (dd, 1H, J_{PH} 14.9 Hz, J_{HH} 2 Hz, PCH_2), 5.31 (dtd, 1H, J_{PH} 426.1 Hz, J_{HH} 2, 10.4 Hz, PH), 7.15 – 7.20 (m, 3 H, Ph), 7.27 – 7.33 (m, 2 H, Ph), 7.35 – 7.45 (m, 18 H, Ar), 7.77 – 7.84 (m, 6H, Ar), 7.86 – 7.94 (m, 6 H, Ar). $^{13}C\{^1H\}$-NMR (CD_2Cl_2): δ_C –2.60 (d, J_{PC} 1.9 Hz, SiMe), –1.72 (d, J_{PC} 2.0 Hz, SiMe), 17.0 (d, J_{PC} 21 Hz, P<u>C</u>H_2), 128.3 (s, CH, Ph), 128.6 (t, J_{PC} 8 Hz, CH, PAr), 129.9 (s, CH, Ph), 130.8 (d, J_{PC} 2 Hz, CH, PAr), 133.7 (dd, J_{PC} 39, 6 Hz, C, PAr), 134.1 (s, CH, Ph), 135.6 (*dd*, J_{PC} 13.5, 1.8 Hz, CH, Ar), 135.7 (dd, J_{PC} 13.8, 1.6 Hz, CH, Ar), 137.5 (d, J_{PC} 4 Hz, C, Ph), 200.0 (*m*, C≡O). $^{31}P\{^1H\}$-NMR: δ_P 22.8 (*dd*, J_{PP} 24, 343 Hz PPh_3), 27.0 (*dd*, J_{PP} 28, 343 Hz, PPh_3), 81.6 (*dd*, J_{PP} 23, 28 Hz, P=C). $^{29}Si\{^1H\}$-NMR: δ_{Si} –2.7. ν_{CO} = 1968 cm^{-1}. Anal. Found: C, 58.62; H, 4.63; Calcd for $C_{46}H_{44}Cl_3OP_3RuSi$: C, 58.70; H, 4.71.

4c (R = tol): ^1H-NMR (CD_2Cl_2): δ_H –0.01 (s, 3H, $SiMe_2$), 0.02 (s, 3H, $SiMe_2$), 0.15 (dm, 1 H, J_{PH} 26.9 Hz, PCH_2), 1.41 (dd, 1H, J_{PH} 14.9 Hz, J_{HH} 1.6 Hz, PCH_2), 2.36 (s, 3H, CH_3), 5.34 (dtm, 1H, J_{PH} 426.4 Hz, J_{HH} 9.3 Hz, PH), 7.02 – 7.07 (m, 2 H, C_6H_4Me), 7.09 – 7.15 (m, 2 H, C_6H_4Me), 7.32 – 7.47 (m, 18 H, PAr), 7.74 – 7.83 (m, 6H, PAr), 7.84 – 7.93 (m, 6 H, PAr). $^{13}C\{^1H\}$-NMR (CD_2Cl_2): δ_C –2.5 (d, J_{PC} 1.7 Hz, SiMe), –1.54 (d, J_{PC} 2.1 Hz, SiMe), 17.1 (d, J_{PC} 21 Hz, P<u>C</u>H_2), 21.8 (s, CH_3), 128.3 (s, CH, tol), 128.5 (t, J_{PC} 8.5 Hz, CH, PAr), 129.1 (s, CH, tol), 133.0 (d, J_{PC} 4 Hz, C, Si-tol-*ipso*), 130.8 (d, J_{PC} 1.7 Hz, CH, PAr), 133.6 (dd, J_{PC} 39, 6 Hz, C, PAr), 133.7 (d, J_{PC} 4 Hz, C, tol), 134.1 (s, CH, tol), 135.6 (*dd*, J_{PC} 14.0, 1.7 Hz, CH, Ar), 135.7 (dd, J_{PC} 14.5, 1.8 Hz, CH, Ar), 139.9 (s, C, *o*-tol), 200.4 (*m*, C≡O). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): δ_P 22.5 (*dd*, J_{PP} 24, 344 Hz PPh_3), 26.4 (*dd*, J_{PP} 27, 343 Hz, PPh_3), 82.4 (*dd*, J_{PP} 24, 27 Hz, P=C). $^{29}Si\{^1H\}$-NMR (CD_2Cl_2): δ_{Si} –2.8. ν_{CO} = 1969 cm^{-1}. Anal. Found: C, 58.98; H, 4.81; Calcd for $C_{47}H_{46}Cl_3OP_3RuSi$: C, 59.10; H, 4.85.

4d (R = $C_6H_4CF_3$-*p*): ^1H-NMR ($CDCl_3$): δ_H 0.02 (s, 3H, $SiMe_2$), 0.05 (s, 3H, $SiMe_2$), 0.19 (dm, 1 H, J_{PH} 25.0 Hz, PCH_2), 1.43 (dd, 1H, J_{PH} 14.7 Hz, J_{HH} 2.5 Hz, PCH_2), 5.21 (dtd, 1H, J_{PH} 428.5 Hz, J_{HH} 10.4, 2.3 Hz PH), 7.21 – 7.27 (m, 2 H, $C_6H_4CF_3$), 7.28 – 7.40 (m, 18 H, PAr), 747 – 7.53 (m, 2 H, $C_6H_4CF_3$), 7.73 – 7.83 (m, 6H, PAr), 7.84 – 7.92 (m, 6 H, PAr). $^{13}C\{^1H\}$-NMR (CD_2Cl_2): δ_C –2.7 (d, J_{PC} 1.5 Hz, SiMe), –2.0 (d, J_{PC} 2.2 Hz, SiMe), 16.5 (d, J_{PC} 21 Hz, P<u>C</u>H_2), 124.3 (q, J_{CF} 274 Hz, CF_3), 124.4 (q, J_{CF} 3.7 Hz, CH, C-*o*-CF_3), 124.5 (q, J_{CF} 3.7 Hz, C, C-*i*-CF_3), 128.1 (dd, J_{PC} 11.6, 9.5 Hz, CH, PAr), 130.3 (dd, J_{PC} 6.7, 1.8 Hz, CH, PAr), 131.1 (td, J_{PC} 8.9, 1.5 Hz, C, $C_6H_4CF_3$), 133.1 (dd, J_{PC} 41, 5 Hz, C, PAr), 134.0 (s, CH, $C_6H_4CF_3$), 135.6 (*td*, J_{PC} 8.7, 1.3 Hz, CH, PAr), 199.3 (*m*, C≡O). $^{31}P\{^1H\}$-NMR: δ_P 22.8 (*dd*, J_{PP} 24, 343 Hz PPh_3), 27.0 (*dd*, J_{PP} 28, 343 Hz, PPh_3), 79.9 (*dd*, J_{PP} 24, 28 Hz, P=C). ^{19}F-NMR (CD_2Cl_2): δ_F –63.0 (s). $^{29}Si\{^1H\}$-NMR (CD_2Cl_2): δ_{Si} –1.9. ν_{CO} = 1968 cm^{-1}. ESI-MS: *m/z* 983.15 [M-Cl].[43]

4e (R = n-Bu): ^1H-NMR ($CDCl_3$): δ_H –0.31 (s, 3H, $SiMe_2$), –0.30 (s, 3H, $SiMe_2$), –0.03 (dm, 1 H, J_{PH} 24.0 Hz, PCH_2),0.18 – 0.24 (m, 2 H, CH_2Si), 0.85 (t, J_{HH} 7.3 Hz, 3 H, $(CH_2)_3CH_3$), 0.94 - 1.03 (m, 2 H, SICH_2), 1.16 – 1.27 (m, 2 H, $SiCH_2CH_2$), 1.42 (dd, 1H, J_{PH} 14.7 Hz, J_{HH} 2.4 Hz, PCH_2), 5.24 (dtd, 1H, J_{PH} 426.5 Hz, J_{HH} 10.8, 1.7 Hz, PH), 7.28 – 7.43 (m, 18 H, PAr), 7.78 – 7.86 (m, 6 H, PAr), 7.92 – 8.00 (m, 6 H, PAr), $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ_C –2.9 (d, J_{PC} 2.6 Hz, SiMe), –2.5 (d, J_{PC} 2.2 Hz, SiMe), 13.9 (s, CH_3), 15.5 (d, J_{PC} 3 Hz, $SiCH_2$), 16.2 (d, J_{PC} 21 Hz, P<u>C</u>H_2), 25.7 (s, <u>C</u>H_2CH_3), 26.5 (s, $SiCH_2$<u>C</u>H_2), 128.1 (dd, J_{PC} 9, 5 Hz, CH, PAr), 130.2 (dd, J_{PC} 4.5, 2.2 Hz, CH, PAr), 131.5 (dd, J_{PC} 41, 5 Hz, C, PAr), 135.6 (*ddd*, J_{PC} 8.8, 4.5, 1.1 Hz, CH, PAr), 199.4 (*m*, C≡O). $^{31}P\{^1H\}$-NMR: δ_P 22.6 (*dd*, J_{PP} 25, 344 Hz PPh_3), 27.2 (*dd*, J_{PP} 28, 344 Hz, PPh_3), 83.3 (*dd*, J_{PP} 24, 28 Hz, P=C). $^{29}Si\{^1H\}$-NMR: δ_{Si} 4.1. ν_{CO} = 1970 cm^{-1}. Anal. Found: C, 57.55; H, 5.10; Calcd for $C_{44}H_{48}Cl_3OP_3RuSi$: C, 57.37; H, 5.25.

Analytical-scale hydrochlorination of [Ru(P=CH^{t}Bu)Cl$_2$(CO)-(PPh$_3$)$_2$]. The reaction was performed on an analytical scale, using a standard solution of crude[44] **1** (35 mg, 4.43 x 10^{-5} mol) in CD_2Cl_2. To a 1/6 aliquot (7.38 x 10^{-6} mol) was added a sub-stoichiometric amount of HCl/Et_2O (1M, 6.5 µl), resulting in formation of **3**, which was identified from its ^{31}P NMR signatures, but not isolated. The addition of a further excess of HCl/Et_2O (ca 20 µl) resulted in loss of **3** and the formation of **6**, which was observed spectroscopically ($^{31}P\{^1H\}$ NMR), but not isolated.

Data for **3**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ_P 16.6 (d, J_{PP} 40.5 Hz), 188.9 (t, J_{PP} 40.5 Hz). ^{31}P NMR (CD_2Cl_2): δ_P 16.6 (br. d, J_{PP} 40.5 Hz), 188.9 (dt, J_{PH} 375.8 Hz, J_{PP} 40 Hz). ^1H NMR ($CDCl_3$): δ_H 0.6 (s, 9 H, t-Bu), 5.38 (dd, J_{PH} 376 Hz, *J* 20 Hz, 1H).

Data for **6**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ_P 21.8 (dd, J_{PP} 346.4, 24.4 Hz), 25.4 (dd, J_{PP} 346.4, 27.0 Hz), 75.4 (dd, J_{PP} 27.0, 24.4 Hz). ^{31}P NMR (CD_2Cl_2): δ_P 16.6 (br. d, J_{PP} 40.5 Hz), 188.9 (dt, J_{PH} 375.8 Hz, J_{PP} 40 Hz).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Computational details and data (including charge distributions and computed energies), NMR figures illustrating the ^{31}P characteristics of compounds **4a-e, 3** and **6**. Plots of ^{31}P-^1H HMBC spectra for **4a-e** illustrating the PPh_3/PH correlations; ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$-NMR figures for compound **4d** indicative of purity (PDF)

DFT optimized geometries for HCl and compounds **1**, **2a**, **3**, **4a**, **6** and intermediary **A** (XYZ)

Crystallographic data for compound **4a** (CCDC 1510476) (CIF)

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Notes

The authors declare no competing financial interest.

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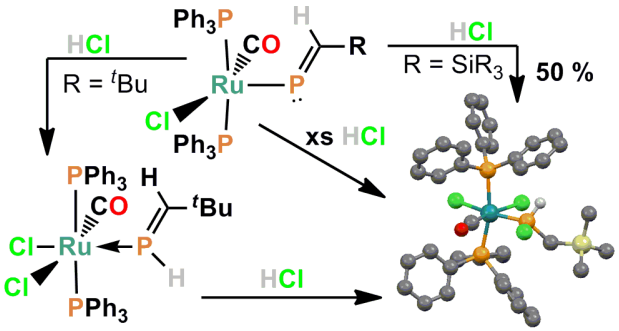
(43) Despite repeated efforts, it has not proven possible to obtain satisfactory microanalysis data for compound **4d**, though only trace organic impurities are apparent from spectroscopic data (see SI), which do permit unequivocal identification. Copies of ^{1}H, ^{13}C, ^{31}P and ^{19}F spectra, are included in SI as evidence of compound purity.

(44) The (limited) available sample of **1** included a second complex, which remains unidentified. The complete consumption of this secondary species with HCl is apparent during the *in situ* conversion of **1** to **3**, the associated resonances remaining unchanged in the presence of excess acid, thus the formation of **6** is confidently assigned to proceed from **3**. The presence of intractable contaminants alongside **3** and **6** respectively precluded their isolation in purity and comprehensive characterization, though their identities can reasonably be asserted from their distinctive ^{31}P NMR signatures.


Ph3P
CO
H
R
HCl
R = tBu
Ru
P
Cl
Ph3P
HCl
R = SiR3
50 %
xs HCl
PPh3
H
CO
tBu
Cl
Ru
P
Cl
H
PPh3
HCl